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Towards a better understanding of the reactive species involved in the photocatalytic degradation of sulfaclozine

Liliane Ismail[a,b,*], Ahmad Rifai[b], Corinne Ferronato[a], Ludovic Fine[a], Farouk Jaber[b,c], Jean-Marc Chovelon[a]

[a] Université Lyon 1, CNRS, UMR 5256, Institut de recherches sur la catalyse et l'environnement de Lyon (IRCELYON), 2 Avenue Albert Einstein, F-69626 Villeurbanne, France
[b] Conseil National de la Recherche Scientifique, Commission Libanaise de l'Energie atomique, Laboratoire d'Analyse des Polluants Organiques, B.P. 11-8281, Riad El Solh, 11072260 Beyrouth, Lebanon
[c] Laboratoire d'Analyse des Composés Organiques (509), Faculté des sciences, Université libanaise, Hadath, Lebanon

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ABSTRACT

The photocatalytic degradation of sulfaclozine on TiO_2 suspensions under UV light was investigated and a complete degradation of 88 μM of sulfaclozine was obtained after 60 min. The addition of isopropanol (500 mM), methanol (500 mM), and KI (10 mM) to the system inhibited the degradation of sulfaclozine c.a 60%, 85% and 95% respectively, which allowed us to conclude that •OH radicals, valence-band holes and electrons could intervene in the degradation of sulfaclozine.

The second order rate constant of the reaction between sulfaclozine and •OH radicals was determined by a competitive kinetics method and a value of (7.2×10^9 M^{-1} s^{-1}) was obtained.

HPLC/DAD and LC–MS/MS analysis were used to identify and follow the appearance and disappearance of sulfaclozine as well as its intermediates. Twelve main intermediates were identified from the photocatalytic degradation of sulfaclozine on TiO_2 suspensions. The comparison of the evolution of those intermediates with and without the addition of methanol showed that the quantity of eight intermediates decreased in the presence of methanol, one intermediate was observed to show an increase, while three others maintained the same amount. These results helped us to propose a tentative mechanism of degradation including •OH radicals, holes, superoxide radicals and electrons attack. In addition, TOC monitoring and mineralization during the photocatalytic degradation of sulfaclozine showed the release of almost all chlorides and the existence of the nitrogen atoms in molecular form even after 180 min of irradiation.

1. Introduction

Antibiotics are widely used in the treatment of human and animal bacterial infections [1,2]. Unfortunately, many of them are not completely metabolized or eliminated in the body and it is estimated that between 30% and 90% [3] are excreted unchanged into the wastewater system. In addition, antibiotics which are biologically active will be poorly eliminated in conventional wastewater treatment plants (WWTP) and, will be so, directly discharged in water streams, and as a consequence antibiotics at a concentration ranging from ng L^{-1} to μg L^{-1} are usually detected in environmental waters [1,4–12]. It is noteworthy here that, even at these low concentrations, antibiotics can cause considerable changes in the biosphere for their high biological activity [13], in addition to the increasing of the probability of bacterial resistance against antibiotics [14–16].

In this context, the use of a complementary treatment such as advanced oxidation processes (AOPs) to remove them from WWTP could be an efficient solution.

These processes are based on the generation of reactive oxygen species (ROS) which cause the degradation of organic pollutants in water.

Among the different AOPs, heterogeneous photocatalysis using TiO_2 as catalyst has emerged as a promising process for eliminating antibiotics from water [17,18]. It is based on the generation of (e^-/h^+) pair leading to the formation of reactive species, such as hydroxyl radicals and superoxide radical anions, when illuminated with photons whose energy is equal or greater than their band-gap energy [19–21].

* Corresponding author at: Université Lyon 1, UMR CNRS 5256, Institut de recherches sur la catalyse et l'environnement de Lyon (IRCELYON), 2 Avenue Albert Einstein, F-69626 Villeurbanne, France. Fax: +33 0 4 72 44 53 99.
E-mail addresses: liliane-isma3il@hotmail.com, liliane.ismail@ircelyon.univ-lyon1.fr (L. Ismail).

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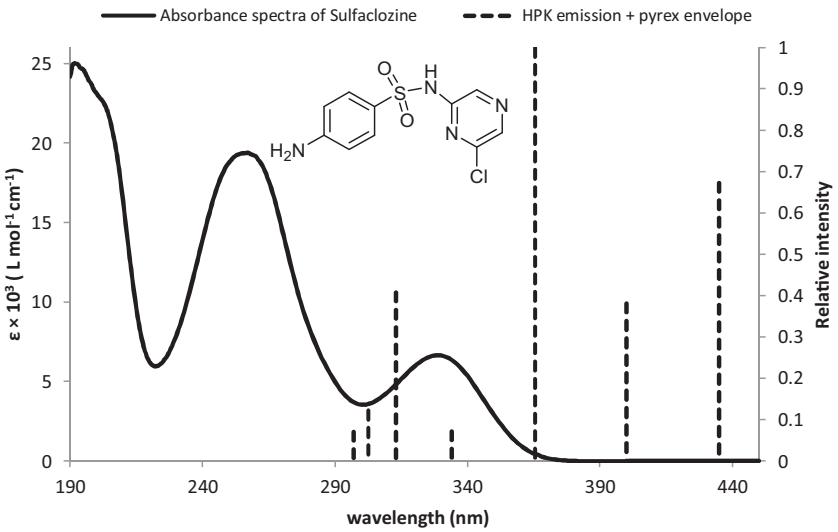


Fig. 1. Organic structure of sulfaclozine, its absorption spectra at pH 7.0 and the emission spectra of the HPK lamp.

The intervention of ROS leading to the initial photoreaction process is not the same in all studies, since the oxidation can proceed through different mechanisms; mainly via •OH radicals mediated pathway and/or by direct electron transfer between the pollutant and the positive holes [19,21,22].

To point out the involvement of ROS, scavengers such as alcohols were used for •OH radicals and/or holes [23–26], whereas iodide for holes, •OH radicals and electrons [23,24,26,27]. In the latter case, the following reactions would take place [24,27].

$$TiO_2 + h\upsilon \rightarrow e^-_{CB} + h^+_{VB}$$

$$h^+_{VB} + I^- \rightarrow I^\bullet$$

$$I^\bullet + e^-_{CB} \rightarrow I^-$$

During photocatalytic degradation of pharmaceutical compounds, intermediate compounds are formed. These compounds might show more toxic effects than the parent compound. Thus, the determination of the extent of mineralization, the identification of photoproducts and the knowledge of the photodegradation pathways and kinetics are essential to predict the behavior and the environmental impact of these pollutants in natural water.

Sulfaclozine (Fig. 1), also known as sulfachloropyrazine, is an oral broad-spectrum sulfonamide antibiotic intended for treatment of various poultry diseases (particularly coccidiosis, fowl typhoid and fowl cholera). Sulfaclozine replace para-aminobenzoic acid (PABA) in the metabolism of protozoa and inhibit their synthesis of folic acid [28]. Moreover, it has been recently found that sulfaclozine is effective against murine toxoplasmosis [29].

This antibiotic when used in veterinary treatments is weakly absorbed from the gastrointestinal tract of animals [28] and thus, it can be excreted intact.

The use of sulfaclozine in animal husbandry can cause its discharge into water cycle through liquid manure or through terrestrial run-off after application of manure. Also, sulfaclozine can reach wastewaters via industrial effluents.

In addition to the toxic effects caused by the accumulation of sulfaclozine in the body, the possibility of developing resistance genes against sulfaclozine is considered to be an emerging threat for the efficiency of such a new promising treatment against toxoplasmosis. Thus, the removal of sulfaclozine from water is important to prevent its toxicity and to ensure its efficiency.

Recently it was found that the application of various AOPs for the elimination of sulfonamides from water such as ultrasound/ozonation process for the elimination of sulfamethoxazole [30], electro-Fenton process for the elimination of sulfachloropyridazine [31], and photolysis for the elimination of sulfapyridine [32], was efficient to remove these compounds. However the determination of the reactive species involved in the degradation process was not studied in detail. So it would be interesting in this study to investigate the photocatalytic degradation of sulfaclozine using TiO_2 as a catalyst and to highlight the role of the different reactive species involved in sulfaclozine photocatalytic degradation.

Thus, the objectives of this study were (a) the evaluation of kinetics aspects of the process (photolysis, adsorption, photocatalysis), (b) the assessment of the intervention of active species by the use of isopropanol, methanol and KI as specific scavengers, (c) the determination of the second-order rate constant of reaction between sulfaclozine and •OH radicals, and (d) the identification of the reaction intermediates as well as their kinetic evolution profiles, with and without methanol, during the process of sulfaclozine photodegradation to understand the mechanistic details of the photodegradation in the UV/TiO_2 process.

2. Materials and methods

2.1. Chemicals and reagents

Sulfaclozine sodium (99% purity) was purchased from Sigma–Aldrich and used as received. Titanium dioxide AEROXIDE TiO_2 P25 was provided by Evonik Degussa (Frankfurt, Germany) with a specific BET area of 50 $m^2\,g^{-1}$ and a mean particle size of 30 nm and crystal distribution of c.a 80% anatase and 20% rutile (properties were given for the suppliers). Polyvinylidene fluoride PVDF filters (0.45 μm) were purchased from Millipore. Acetonitrile, methanol, isopropanol (LC–MS/MS grade), potassium iodide, benzoic acid, sulfuric acid, formic acid, iron (II) sulfate, H_2O_2, NaOH, HCl and perchloric acid were purchased from Sigma–Aldrich. Other reagents were at least of analytical grade.

Ultra pure water was obtained from Thermo scientific (easy pure II) water purification system.

2.2. Photocatalytic procedure

The adsorption and illumination of sulfaclozine was carried out in an open Pyrex glass reactor (cut-off at 295 nm, 4 cm diameter,

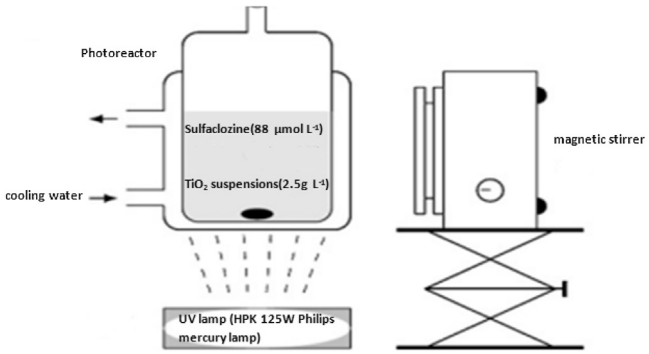


Fig. 2. Scheme of experimental setup.

9 cm height) with a double walled cooling water jacket to keep the temperature of solutions constant throughout the experiments (20 °C). The reactor is equipped with a magnetic stirring bar (Fig. 2).

The light source was a HPK 125 W Philips mercury lamp with main emission wavelength at 365 nm, cooled with a water circulation. The radiant flux entering the irradiation cell was measured by a VLX-3W radiometer with CX-365 detector (UV-A) and a value of 4 mW cm^{-2} was found at the walls of the reactor. Prior to illumination, an aqueous solution of 25 mL of sulfaclozine $C_0 = 25\ mg\ L^{-1}$ (88 µmol L^{-1}) with 2.5 g L^{-1} TiO_2 suspensions was magnetically stirred in the dark for 20 min to reach the adsorption–desorption equilibrium. Then the UV light was turned on for the photocatalytic degradation experiments. One first sample was taken out at the end of the dark adsorption period just before turning on the irradiation, in order to determine the bulk sulfaclozine concentration. This value was taken as the initial concentration for the photocatalytic experiment, denoted hereafter as C_{eq} . During irradiation, samples were with-drawn regularly from the reactor and filtered immediately through 0.45 µm PVDF membrane filters to remove TiO_2 particles.

It should be noted that most of the measurements were repeated up to 3 times and the error for those repeated was less than 5%.

2.3. Analytical procedures

2.3.1. HPLC-DAD

A Shimadzu HPLC (Shimadzu, Kyoto, Japan) equipped with a photodiode array detector was used to monitor the concentration of the parent molecule. A 20 µL of filtered irradiated samples was directly injected. Analytical separation was performed using a DIONEX C18 column (250 mm × 4.6 mm, particle size 5 µm) with mobile phase 80% water at pH 3.0 (adjusted with formic acid) and 20% ACN at flow rate of 0.8 mL min^{-1}. The detection wavelength was 271 nm, corresponding to λ_{max} of sulfaclozine at pH 3.0.

2.3.2. LC–MS/MS

The identification of degradation intermediates of sulfaclozine and their evolution were carried out by using LC–MS/MS. The LC system was interfaced to an Agilent 6410 triple quadrupole mass spectrometer (Agilent technologies, USA) via electrospray ionization (ESI) source and it was operated in positive mode using high purity nitrogen gas as a collision gas and also as nebulization gas at 30 and 40 psi respectively. The source temperature was maintained at 350 °C and the separation was carried out on a DIONEX C18 column (250 mm × 4.6 mm, particle size 5 µm) with mobile phase 80% water at pH 3.0 (adjusted with formic acid) and 20% ACN at flow rate of 0.7 mL min^{-1}.

Furthermore, the appearance and disappearance of different intermediates was analyzed by LC–MS/MS in SIM mode. For that, aliquots were taken at regular time intervals during irradiation and after filtration to separate the TiO_2 particles.

2.3.3. Ionic chromatography

A Metrohm 930 IC Flex (Metrohm, Herisau, Switzerland) equipped with chemical suppression and a conductimeter detector was used. For cations, the analysis was performed by using a Metrohm Metrosep C6 column (150 mm × 4 mm) at 30 °C with a mobile phase made up of 1.7 mM nitric acid and 1.7 mM NaOH dipicolinic acid as eluent at a flow rate of 0.9 mL min^{-1}. The analysis of anions was performed by using a Metrosep A supp 5 column (150 mm × 4 mm) at 40 °C with 5 mM Na_2CO_3 and 0.3 mM NaOH as eluent at a flow of 0.8 mL min^{-1}.

2.3.4. Total organic carbon analysis

TOC-L Shimadzu (Shimadzu, Kyoto, Japan) was used for the determination of the extent of mineralization during photacatalysis of sulfaclozine. TOC measurements were carried out on filtered irradiated samples of sulfaclozine (25 mg L^{-1}) and calibration was achieved with potassium hydrogen phthalate standard.

2.4. Determination of pKa_2 of sulfaclozine

Absorption spectra of sulfaclozine at different pHs were plotted using Agilent 8453 UV–vis Spectrophotometer (Agilent technologies, USA). The pH of the solutions was adjusted by adding NaOH or HCl and absorption spectra were immediately carried out to prevent any hydrolysis reactions. Differences in absorbance at a single wavelength were plotted as a function of pH and pKa_2 of sulfaclozine was deduced from the inflection point.

2.5. Determination of second-order rate constant of sulfaclozine reacting with •OH radicals

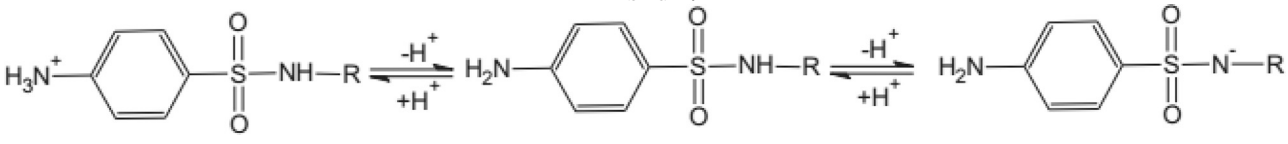
The second-order rate constant of •OH radicals and sulfaclozine reaction was determined by using Fenton's reagent to generate •OH radicals. Benzoic acid, for which its rate constant with •OH is known ($k_{\bullet OH,BA} = 5.9 \times 10^9\ M^{-1}\ s^{-1}$) [33], was used as reference compound in this study. The initial solution contained 88 µM benzoic acid, 88 µM sulfaclozine, 0.2 mM Fe^{2+} and 0.5 mM H_2O_2 at pH = 3.5 (adjusted by sulfuric acid) at room temperature (20 °C). The reactor was wrapped in aluminum foil to exclude light and prevent photo-Fenton chemistry. Samples (0.5 mL) were withdrawn at predetermined intervals, and the reactions were quenched with an equivalent volume of methanol. Then, samples were analyzed via HPLC-DAD to determine the concentrations of sulfaclozine and benzoic acid.

3. Results and discussion

3.1. Preliminary experiments

3.1.1. Determination of pKa_2 of sulfaclozine

Sulfonamides generally have two acid-base dissociation equilibrium:



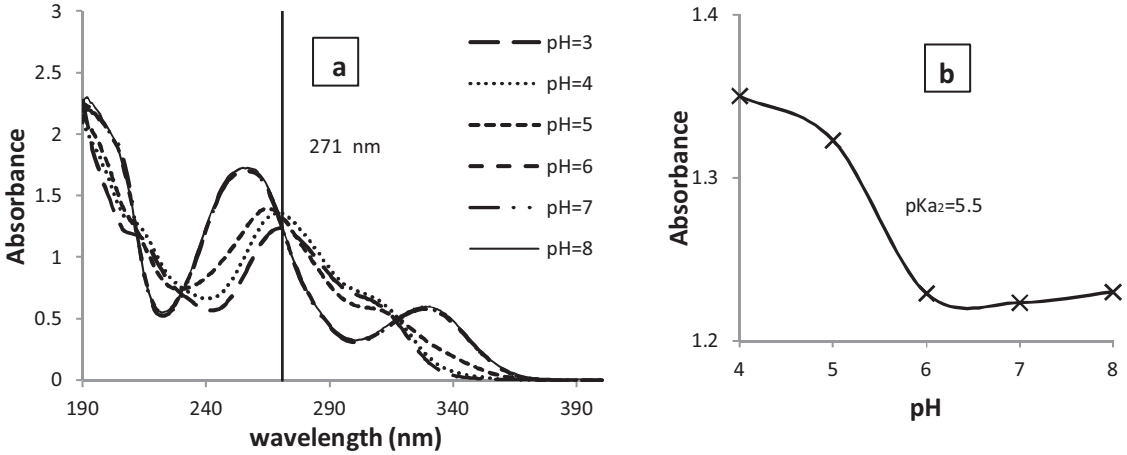


Fig. 3. (a) Absorption spectra of 25 mg L^{-1} sulfaclozine at selected pH values, the absorption spectrum overlaps at pH > 6, (b) Absorbance values of sulfaclozine at 271 nm plotted as a function of pH.

pKa_1 is almost the same for all this kind of sulfonamides (≈2) because, at low pH, the protonation takes place on NH_2 group of the aniline ring common for this class of sulfonamides, while the second protolytic dissociation (pKa_2) takes place on SO_2-NH-R group which varies from a sulfonamide to another depending on the substituent of each sulfonamide [34–36]. To determine the pKa_2 of sulfaclozine, the absorbance values at 271 nm were plotted as a function of pH (Fig. 3a). The pKa_2 obtained from the inflection point was 5.5 (Fig. 3b).

3.1.2. Effect of pH on the hydrolysis of sulfaclozine

Experiments showed that the pH has an effect on the hydrolysis of sulfaclozine in water (C_0 of 25 mg L^{-1}): At pH 7.0 and pH 11.0 no hydrolysis of sulfaclozine was observed, while at acidic pH, a noticeable decay of sulfaclozine due to hydrolysis occurred. For example, at pH 5.0 and pH 3.0 a decrease of 19% and 28%, respectively, of an initial concentration of sulfaclozine was observed after 60 min (temperature = 20 °C).

3.1.3. Photolysis, adsorption and photocatalysis of sulfaclozine

Fig. 4 shows the behavior of sulfaclozine towards three different processes at an initial pH of 7:

(1) Photolysis: the photodegradation of 25 mg L^{-1} of sulfaclozine, with UV-light and without any catalyst, was evaluated: the initial concentration of sulfaclozine decreased slightly (1% in 60 min). Since the photolysis is based on the degradation of organic compounds by direct absorption of photons, the weak photolysis of sulfaclozine can be attributed i/to a low overlapping between sulfaclozine UV–vis absorbance spectrum and the filtered HPK lamp emission spectrum (Fig. 1) and ii/to a low quantum yield of degradation. Thus, we can conclude that, under these experimental conditions, photodegradation would not compete with photocatalysis.
(2) Adsorption: A solution of 25 mg L^{-1} of sulfaclozine was stirred in the dark with TiO_2 suspensions (2.5 g L^{-1}). After 20 min of continuous stirring, a slight decrease of sulfaclozine concentration (3%) due to the adsorption was observed which remained steady after that, corresponding to an adsorption–desorption

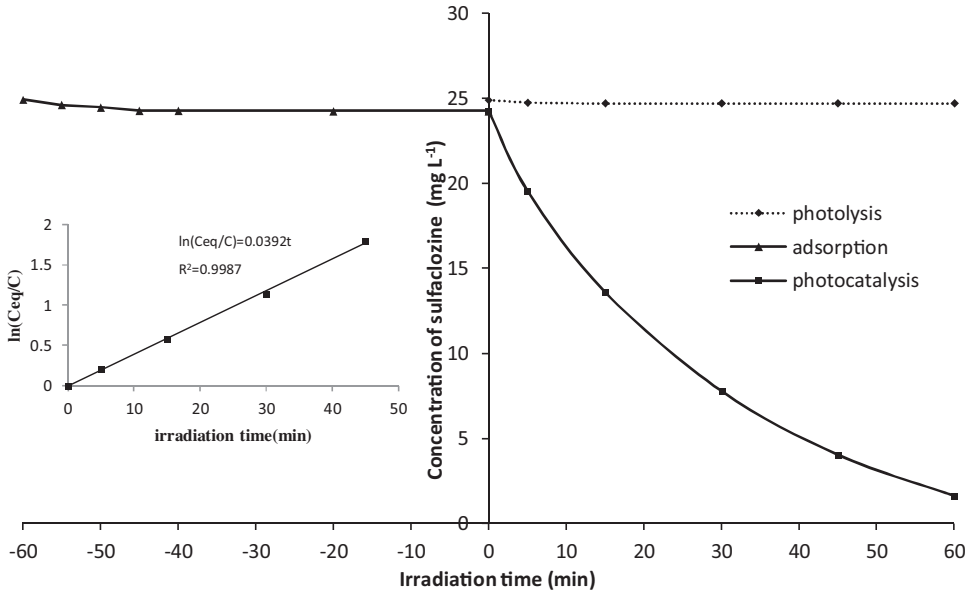


Fig. 4. Photolysis, adsorption, photocatalysis, of sulfaclozine (25 mg L^{-1}) at pH 7.0. Inset: The linear transformation of ln (Ceq/C) = f(t) for the photocatalytic transformation of sulfaclozine.

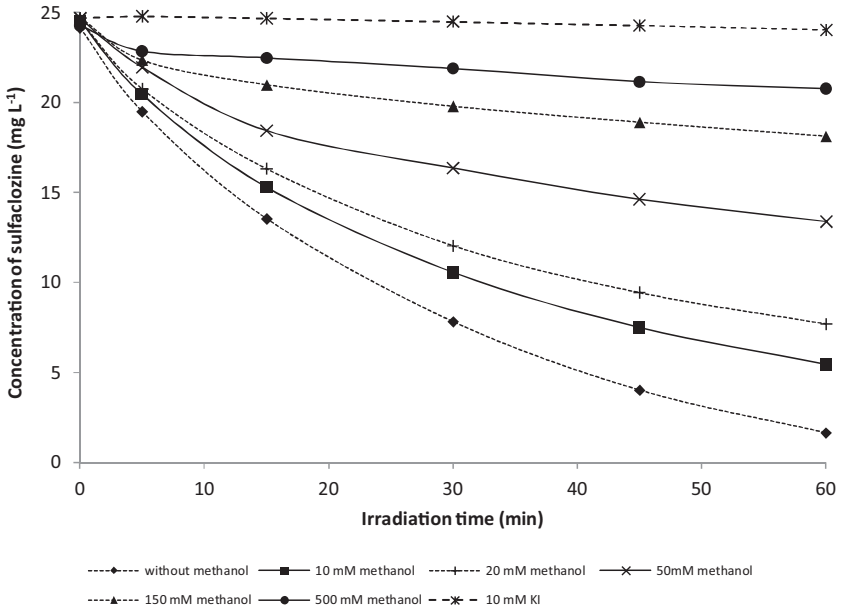


Fig. 5. Effect of KI and methanol concentration on the inhibition of photocatalytic degradation of sulfaclozine (initial concentration of sulfaclozine = 25 mg L^{-1}, TiO_2 dose = 2.5 g L^{-1}, initial pH 7).

equilibrium. The adsorption of sulfaclozine on TiO_2 surface depends on pH since the TiO_2 surface is positively charged when $pH < pH_{pzc}$: Ti-OH + $H^+ \rightarrow TiOH_2^+$; and negatively charged when $pH > pH_{pzc}$: Ti-OH + $OH^- \rightarrow TiO^- + H_2O$.

As a consequence, at pH 7.0, a weak adsorption was observed, since both TiO_2 ($pH > pH_{pzc}$) and sulfaclozine ($pH > pKa_2$) are rather negatively charged, provoking electrostatic repulsion between them (pH_{pzc} = 6.3 and pKa_2 = 5.5).

(3) Photocatalysis: the degradation of 25 mg L^{-1} of sulfaclozine on TiO_2 (2.5 g L^{-1}) suspensions under UV-light was followed and a complete disappearance of sulfaclozine was reached after 60 min. The noticeable photocatalytic degradation of sulfaclozine was most likely due to the mediation of TiO_2 and to the formation of ROS, such as hydroxyl radical (•OH) and/or positive valence band holes.

The photocatalytic degradation of sulfaclozine can be, in a first approach, described by a pseudo-first-order kinetic model [37,38]. In the inset of Fig. 4 the logarithm of the ratio of the concentration after sorption–desorption equilibrium (C_{eq}) to the concentration (C) at a given time versus time (t) is plotted and the rate-constant of sulfaclozine photodegradation was determined to be equal to 0.039 min^{-1}.

3.1.4. Determination of the different reactive species involved in the photocatalytic degradation of sulfaclozine

During photocatalytic degradation reaction, oxidation process is triggered by the generation of photoelectrons and photoholes. In addition to a direct oxidation of pollutant molecules by positive valence band holes, an oxidation via ROS (•OH; $•O_2^-$; $•HO_2$ and H_2O_2) can also take place.

In order to assess the contribution of •OH radicals, photoholes and electrons in the photocatalytic degradation, specific scavengers were used such as isopropanol, methanol and KI.

3.1.5. Effect of methanol

Methanol is used as a scavenger for both holes and •OH radicals [39–41] ($k_{MeOH,•OH} = 9.7 \times 10^8$ M^{-1} s^{-1}) [23]. The effect of different concentrations of methanol on the photocatalytic degradation of sulfaclozine is shown in Fig. 5. An increasing concentration of methanol leads to an increase in the inhibition percentage of the degradation of sulfaclozine to reach 85% after 45 min of irradiation when [MeOH] = 500 mM. This result suggested that valance-band holes and •OH radicals are highly involved in the degradation of sulfaclozine. For a better comprehension, other experiments using isopropanol were carried out.

3.1.6. Effect of isopropanol

Isopropanol has a higher reaction rate with•OH radicals than methanol ($k_{i\text{-}PrOH,•OH} = 1.9 \times 10^9$ $M^{-1}s^{-1}$) [42] and is well used as •OH radicals scavenger. It is widely used in photocatalysis to discriminate the direct oxidation of substrates by holes or by •OH radicals [42–44].

The effect of different concentrations of isopropanol is showed in Fig. 6: It was found that an increasing concentration of isopropanol leads to an increase in the inhibition of percentage degradation of sulfaclozine to reach 60% after 45 min of irradiation when [isopropanol] = 500 mM.

The lower inhibition percentage obtained with isopropanol with respect to methanol could confirm the intervention of valence-band holes in the mechanism of degradation of sulfaclozine in addition to •OH radicals.

3.1.7. Effect of KI

Iodide ion can be used to evaluate the contribution of •OH radicals, photogenerated holes and electrons in the degradation. Therefore, experiments with KI (10 mM) to study its effect on the degradation of sulfaclozine were performed and an inhibition of 95% of the photocatalytic degradation was observed (Fig. 5). The percentage of degradation with KI was higher than that obtained with methanol leading to the conclusion that electrons could also be involved in the mechanism of degradation of sulfaclozine.

To better understand the role of •OH radicals in the degradation of sulfaclozine, the second order rate constant of reaction between sulfaclozine and•OH radicals was determined to confirm this result.

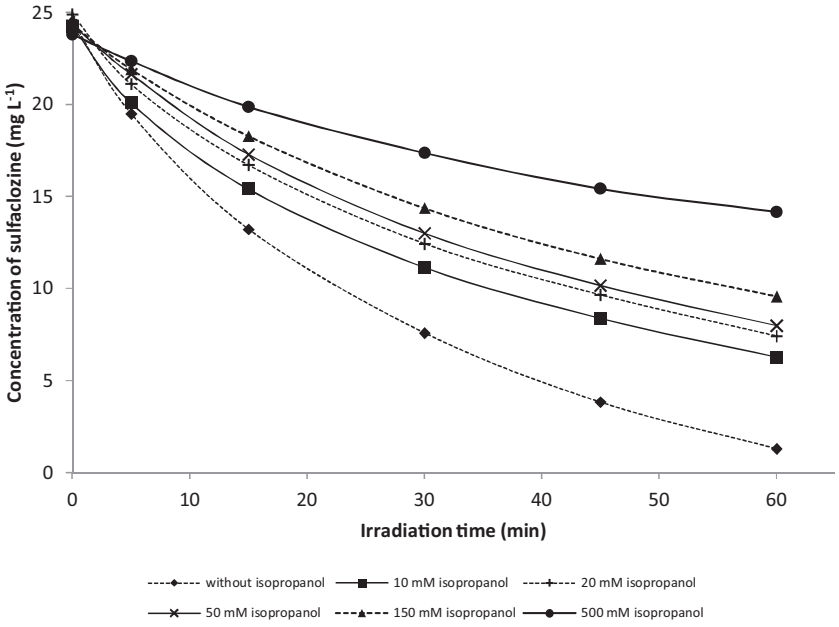


Fig. 6. Effect of isopropanol concentration on the inhibition of photocatalytic degradation of sulfaclozine (initial concentration of sulfaclozine = 25 mg L^{-1}, TiO_2 dose = 2.5 g L^{-1}, initial pH 7).

3.2. Determination of the second-order rate constant of reaction between sulfaclozine and •OH radicals

Kinetically, the reaction between •OH radicals and organic substrates (S) follows a second order: first order with respect to the concentration of organic compound and first order with respect to the concentration of •OH radicals. The rate of disappearance of an organic substrate S can be then expressed:

$-(d[S])/dt = k_{\bullet OH,S}[OH][S]$, where $k_{\bullet OH,S}$ is the rate constant for the reaction between S and •OH

The reaction which generates hydroxyl radicals is the limiting step in the oxidation of most organic compounds, since this reaction is relatively slow compared to the consumption of •OH radicals by organic compounds, intermediates and by photoproducts formed. Since •OH radicals are slowly generated and quickly consumed (10^7–10^{10} mol^{-1} L s^{-1}), their concentration is maintained almost the same in the solution (steady state) and the rate of the reaction can be described by an apparent kinetic law of order 1 with respect to the concentration of organic compounds:

$$-(d[\bullet OH])/dt = 0$$

$$-(d[S])/dt = k_{app}[S]$$

We can write:

$$\ln(S_t/S_0) = -k_{app}.t$$

With $k_{app} = k_{\bullet OH,S}[\bullet OH]$

Monitoring the disappearance of the substrate S as a function of time, allows estimating experimentally the apparent constant rate of the reaction of pseudo-first order. The absolute rate constant of the reaction between •OH radicals and organic substrate of order 2 can be then determined by the method of competitive kinetics, by setting competition constant k_s of the substrate S to be determined with a reference R compound whose kinetic constant is known [34,45]. Therefore, the variations in concentrations over time are given by:

$$-(d[S])/dt = k_{\bullet OH,S}[\bullet OH][S]$$

$$-(d[R])/dt = k_{\bullet OH,R}[\bullet OH][R]$$

and $\ln([S]_0/[S]_t) = k_{(\bullet OH,S)}/k_{(\bullet OH,R)} \times \ln([R]_0/[R]_t)$

This method was used in our study and the second order reaction of sulfaclozine (SCL) reacting with •OH was quantified using Fenton's reagent as •OH generator and benzoic acid (BA) as a reference compound ($k_{\bullet OH,BA} = 5.9 \times 10^9$ M^{-1} s^{-1}).

$\ln([SCL]_0/[SCL]_t) = k_{(\bullet OH,SCL)}/k_{(\bullet OH,BA)} \times \ln([BA]_0/[BA]_t)$

The reaction rate constant was then calculated by plotting $\ln([SCL]_0/[SCL]_t)$ versus $\ln([BA]_0/[BA]_t)$ (Fig. 7) and a calculated $k_{\bullet OH,SCL}$ value of 7.2×10^9 M^{-1} s^{-1} was found. This high value for the second-order kinetic rate constant confirms that •OH is the primary reactive species involved in the photocatalytic degradation of sulfaclozine on TiO_2 suspensions.

Interestingly, this value is very close to that reported for the hydroxylation of other sulfonamide antibiotics (5×10^9 M^{-1} s^{-1} for sulfamethazine, 3.8×10^9 M^{-1} s^{-1} for sulfamerazine, 3.7×10^9 M^{-1} s^{-1} for sulfadiazine, 4.4×10^9 M^{-1} s^{-1} for sulfachlororopyridazine and 6.1×10^9 M^{-1} s^{-1} for sulfadimethoxine)

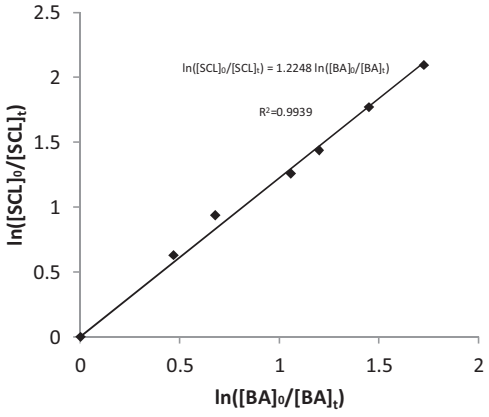
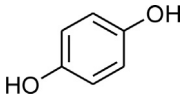
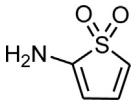
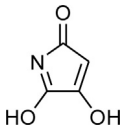
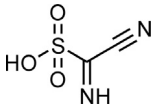
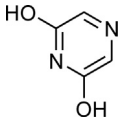
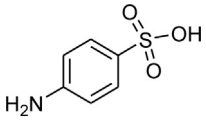
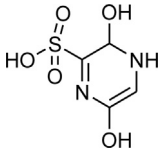
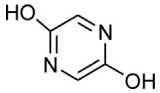
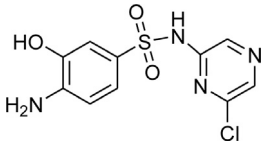
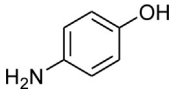
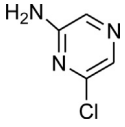
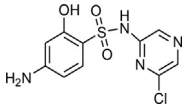
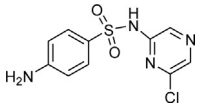


Fig. 7. Determination of second-order constant rate of sulfaclozine reacting with •OH radicals.

Table 1
Pseudo-molecular ions (MH^+), retention time, main MS/MS transitions recorded in LC- ESI(+)- MS/MS and chemical structure for by-products of sulfaclozine.

N°	$[M+H]^+$	Retention time (minutes)	Positive fragments	Proposed structure
1	111	3.6	91, 82, 76	
2	132	3.65	114, 104	
3	114	3.75	96, 72	
4	135	3.9	89, 75, 62	
5	113	3.95	70, 63	
6	174	4.35	156, 133, 107, 100, 92	
7	195	4.35	150, 117, 108	
8	113	4.55	72, 63	
9	301	5.2	246, 237, 195, 172, 130, 108	
10	110	5.2	93, 69	
11	130	6.15	103, 89, 61	
12	301	11.4	172, 130, 124, 108	
13	285 (sulfaclozine)	14.9	156, 130, 108, 92	

[34], since the hydroxylation took place on the aniline ring (see mechanism), common for these sulfonamides.

3.3. Intermediates identification and proposition for a mechanism of degradation

3.3.1. Identification of organic by-products structures

In order to determine the structure of intermediates of sulfaclozine (*MW* 284 amu), a mixture of solutions collected at 0, 5, 15, 30, 45, 60, 90 and 120 min of degradation was analyzed. The characterization of intermediates was performed on LC-Triple Quadrupole using three different analysis modes: SIM-SCAN, neutral loss and identification of the precursor ion. The second and the third modes helped in the identification of transitions which facilitates the proposition of intermediate structures. Due to the lack and/or the weakness of the response in ESI-negative ionization mode, only the ESI positive ionization mode was used. In addition, the number of chlorine and nitrogen atoms remaining in each photoproduct structure was easily determined on the basis of isotopic distributions and the nitrogen rule [46,47].

Table 1 presents the pseudo molecular ions, retention time, positive fragments and the structure proposed for the 12 main intermediates tentatively identified under these conditions. Their molecular weights (MWs) were readily determined by the presence of two peaks separated by 22 amu, corresponding to the protonated molecule MH^+ and an adduct of sodium cations $[M+Na]^+$.

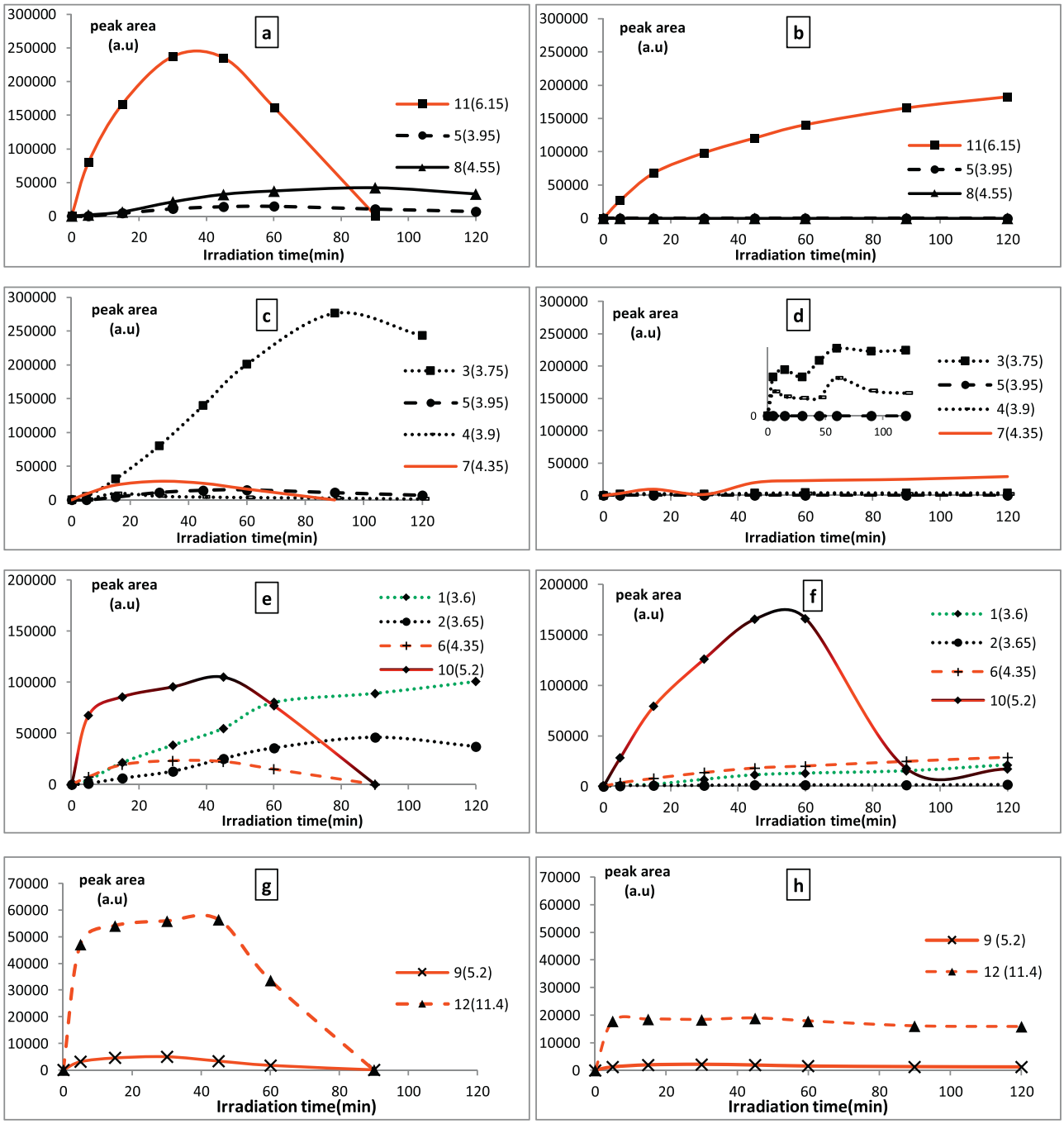


Fig. 8. Evolution of main photoproducts in the absence (a, c, e, g) and in the presence of methanol 150 mM (b, d, f, h) versus irradiation time (initial concentration of sulfaclozine = 25 mg L^{-1}, TiO_2 dose = 2.5 g L^{-1}, initial pH 7).

Some fragmentation mechanisms were described in the part 3.3.4.

3.3.2. Kinetic study

A kinetic study carried out during the course of the degradation was followed to better understand the mechanism of the degradation. Fig. 8(a, c, e and g) shows the abundances of intermediates estimated by integrating their chromatographic peaks on the total ion current (TIC) by using an arbitrary unit. An accurate quantification of intermediates was not possible considering the absence of standards. The abundance of sulfaclozine was not plotted in the figure because it was out of scale. Furthermore, less than 10% of the initial quantity of sulfaclozine was detected after 60 min of irradiation.

Among the 12 detected photoproducts, the compounds 1, 2, 3, 5 and 8 can be considered as second generation intermediates since they are not formed as soon as the irradiation starts, but their intensity increases while the intensity of the compounds 10, 6, 7 and 11, respectively, decreases.

3.3.3. Comparison of the evolution of by-products with and without methanol

In order to confirm the contribution of different reactive species in the photocatalytic degradation of sulfaclozine, the evolution of intermediates after addition of 150 mM of methanol was plotted Fig. 8(b, d, f and h). From this figure we can conclude that the same intermediates were obtained with and without methanol but with different quantities.

For example Fig. 8 shows that the abundance of products 1, 2, 3, 4, 5, 8, 9 and 12 were lower in presence of methanol which confirms that the mechanism of degradation of sulfaclozine implies holes and/or •OH radicals. On the other hand, for products 6, 7 and 11, the same abundances with and without methanol were obtained and the formation of product 10 was even enhanced after the addition of methanol. Hence, their formation would not necessary involve holes or •OH radicals and other reactive species have to be proposed. For example for products 6 and 11 it was suggested by Hu et al. for the degradation of sulfamethoxazole a redox reaction involving electrons [17] as well as by Calza et al. for other sulfonamides [48]. On the other hand, since the conduction band electrons can react with oxygen adsorbed on TiO_2 to lead to the formation of $O_2^{\bullet -}$, we can assume that this latter species could also be involved in the sulfaclozine degradation to obtain the products 6 and 10. Recently, Ding et al. [12] have shown that $O_2^{\bullet -}$ could be responsible of the mineralization of sulfamethoxazole by attacking on the sulfone moiety which causes, the cleavage of the S—N bond. In addition, Diaz et al. [49] used sulpha drugs for scavenging photogenerated singlet molecular oxygen and superoxide radical anion.

All these results could explain why we did not observe 100% of inhibition in presence of a high amount of methanol.

Furthermore, it seems that the degradation of products 6, 7, 9, 11 and 12 needs the intervention of holes and/or •OH radicals since these compounds are no longer degraded.

3.3.4. Proposition of degradation mechanism

Compounds 9 and 12 have molecular weight (*MW*) equal to 300 amu. Their structure came from hydroxylation of sulfaclozine on aniline ring, noting that many publications stated the hydroxylation is the first stage in photodegradation of organic compounds [31,43,50]. Dirany et al. [31] found in their study a degradation product for sulfachloropyridazine with the same *MW* 300 and explained the structure by the addition of •OH on the aniline ring, as well as the proposition of Fabianska et al. [51], Guo et al. [30], Kin et al. [52] for sulfonamides degradation.

The stucture of compound 11 came from oxido/reductive attack of S—N bond with the breaking of the molecule. This compound with a *MW* of 129 amu is 6-chloropyrazin-2-amine [48]. $11H^+$ gives by dissociation the ions with *m*/*z* 103, 89 and 61. These ions were explained by losing HCN, $CHCNH_2$, and $(H_2N)(CN)CNH$, and from the pseudo-molecular ion, respectively.

Compound 6 (*MW* 173 amu) is the structure of the sulfanilic acid [51,53]. This compound could come either from the hydroxylation of the second part of the molecule formed with the compound 11 or from an attack of $O_2^{\bullet -}$ on the sulfone derivative [12]. By MS/MS, $6H^+$ eliminates water molecule and $CHCNH_2$ to obtain the ions with *m*/*z* 156 and 133, respectively. The second elimination is followed by the loss of 26 amu as CHCH for observing the ion *m*/*z* 107.

Compound 10 (*MW* 109 amu) could be obtained from compound 6 by an attack of $O_2^{\bullet -}$ on the sulfone derivative [12] or from the elimination of SO_2 provoked by a h+ attack [54] or from the hydroxylation of the aniline ring in sulfaclozine [31]. This interpretation emerged from the minor augmentation of the kinetic curve of the compound 10 in the same time of the disappearance of compound 6 (Fig. 8). Fabianska et al. obtained the same product from the electrochemical degradation of sulfonamides [51]. The structure proposed was explained by the fragments obtained by MS/MS which $10H^+$ with *m*/*z* 110 eliminates NH_3 (17 amu) and $CHCNH_2$ (41 amu) for giving the ions with *m*/*z* 93 and 69, respectively.

The second part of sulfaclozine obtained from the formation of compound 10 was the radical *N*-(6-chloropyrazin-2-yl) sulfonamide. This structure realized 1,3-rearrangement [55,56] followed by the hydroxylation and the elimination of NH_3 by the addition of two hydrogen radicals. These steps are followed by replacing the chlorine atom by radical hydroxyl and the addition of water molecule whose addition is familiar in photochemistry [57] to obtain the structure of the compound 7. The mechanism of the formation of compound 7 was presented in Fig. 9. The position of water molecule addition was explicated by transition. The 7H+ with *m*/*z*

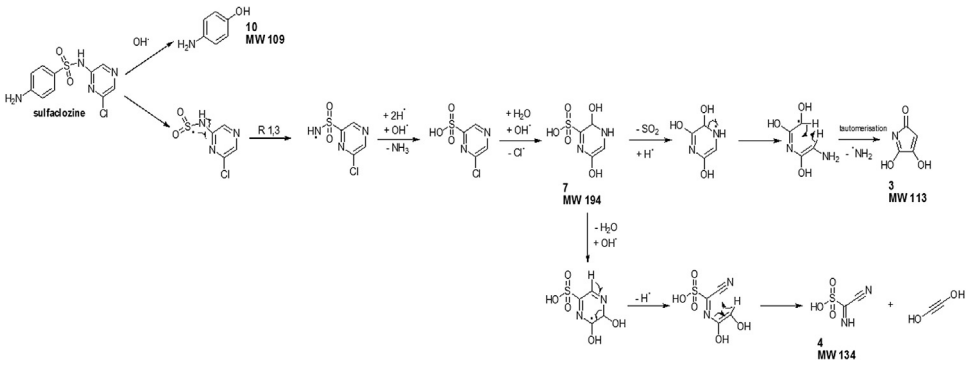


Fig. 9. Mechanisms postulated for the formation of compounds 3, 4, 7 and 10 from irradiated sulfaclozine.

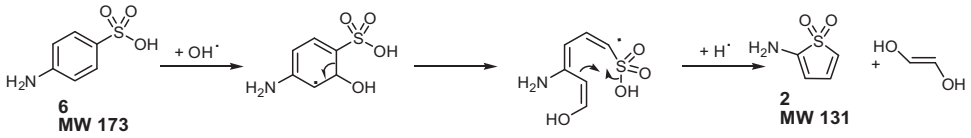


Fig. 10. Mechanisms postulated for the formation of compound 2 from compound 6.

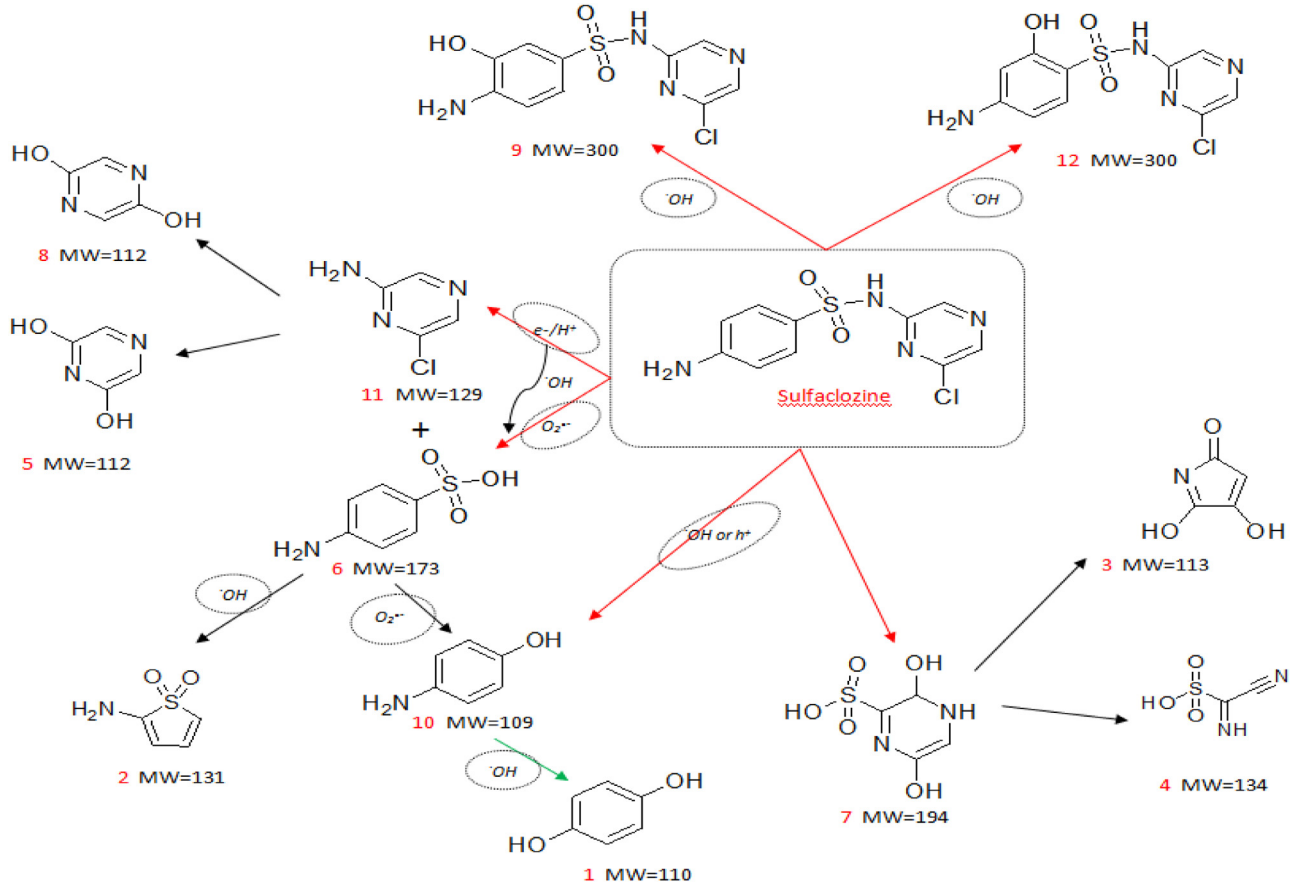


Fig. 11. Photocatalytic degradation pathway of sulfaclozine.

195 eliminated NHCHOH and 1,2-dihydroazete-2,3-diol to obtain the ions fragments with *m*/*z* 150 and 108, respectively.

The compound 5 was obtained from replacing chlorine and NH_2 by bi-hydroxyl radical in the structure of compound 11. By MSMS, $5H^+$ loses 43 amu (HOCN) for giving the ion with *m*/*z* 70. Compound 8 has the same *MW* 112 as compound 5 but the difference relies on the position of the two hydroxyls. In 5, a meta- position is assumed while in 8 it would rather be at para-position since, by MSMS, only the structure of $8H^+$ could eliminate the OHCCH (42 amu) to give the ion with *m*/*z* 72.

The elimination of SO_2 followed by the addition of hydrogen radical on the structure of compound 7 leads to the production of a radical molecule. By opening the cycle, cyclic structure was formed by dihydrogen molecule elimination at 6 centers in the structure. These steps were followed by the tautomerisation of hydroxyl to ketone form and elimination of NH_2 radical to obtain the structure of the compound 3. The ion fragments shown in MS/MS were explained by the elimination of water molecule and HOCCH from the pseudo molecular ion $3H^+$, respectively. The proposed mechanism for the formation of compounds 3, 4, 7 and 10 were presented in Fig. 9.

The hydroxylation of compound 6 followed by different rearrangement led to the loss of ethene-1,2-diol and the formation of a cyclic structure. It was followed by the addition of hydrogen radical to obtain the structure of the compound 2. The pathway was presented in Fig. 10.

All these data allowed us to propose a mechanism of degradation of sulfaclozine shown in Fig. 11.

3.4. Evolution of mineralization

Mineralization is a potential end-point for decomposition of organic material. The goal of treatment processes should be complete mineralization of the pollutant into CO_2, H_2O and inorganic ions (such as nitrates and/or ammoniums, sulfates, chlorides in the case of sulfaclozine) rather than just removal of the parent compound. Therefore, the extent of mineralization during the photocatalytic degradation of sulfaclozine was determined in Fig. 12. It was observed that TOC removal proceeded much more slowly compared to the degradation of sulfaclozine. 75% of TOC removal was observed after 180 min of irradiation, implying that complete mineralization could be obtained at a longer time of photocatalysis. For chloride ions, 87% was released after 180 min of irradiation, meaning that almost all chlorides were released in the solution. For sulfates, the expected stoechiometric quantity was not reached since only 37% of sulfate is present in the solution. This result can be

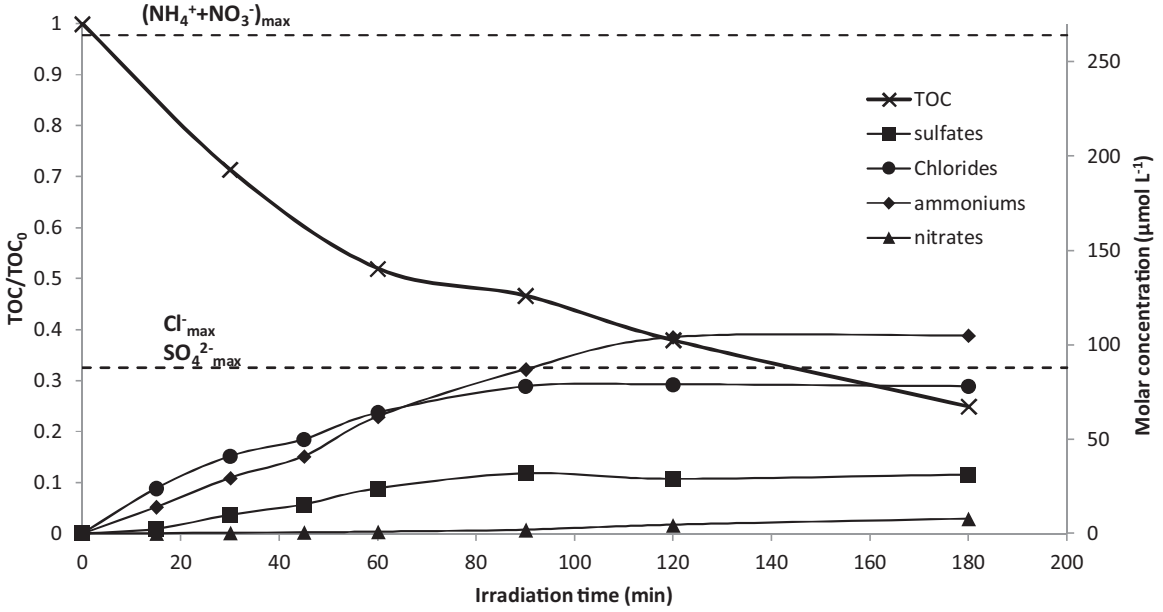


Fig. 12. Evolution of TOC, sulfates, chlorides, ammoniums and nitrates in the solution during the photocatalytic degradation of sulfaclozine.

explained by the partially irreversible adsorption of SO_4^{2-} ions at the surface of TiO_2 as already observed [54,58] since the pH of the solution after 180 min of irradiation has a value of 3 which means that the surface of TiO_2 would be positively charged. Nitrogen in sulfaclozine was released as ammonium and nitrate ions. After 180 min of irradiation only 47% of the stochiometric amount of total releasable nitrogen was released which could be explained by the fact that some of the N-containing intermediates may remain in stable molecular forms as suggested by Calza et al. [48]. This result can be confirmed by the occurrence of photoproducts containing nitrogen atoms (2, 3 and 8) even after 120 min of irradiation (see Fig. 8).

4. Conclusions

UV-TiO_2 photocatalysis was shown to be an efficient technique for eliminating sulfaclozine from water. A detailed study on its photocatalytic degradation (kinetics, influence of scavengers with regard to ROS, intermediates identification, and proposed pathway) was presented. It was shown that 94% of sulfaclozine disappeared after 60 min of illumination, while the presence of isopropanol (500 mM), methanol (500 mM), and KI (10 mM) in the solution inhibited its degradation c.a 60, 85 and 95% respectively which means that •OH radicals, holes and electrons are involved in the degradation mechanism. In this paper it was observed that the use of scavengers could give relevant information about the involved species in heterogeneous photocatalysis which can aid in proposing a tentative pathway mechanism. In addition, it was confirmed that •OH radicals were strongly involved in the sulfaclozine degradation since a high second order rate constant with sulfaclozine ($k = 7.2 \times 10^9\ M^{-1}\ s^{-1}$) was obtained using a competitive kinetic method. Moreover, $O_2^{\bullet -}$ radicals were found to play a role in the photocatalytic degradation of sulfaclozine.

The monitoring of mineralization showed an elimination of 75% of TOC in 180 min. The release of almost all chlorides was observed whereas nitrogen atoms still existed in molecular forms after 180 min of irradiation.

Acknowledgments

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